LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

UCRL-TR-201998

Final report summary of LDRD 02-LW-022 “Quantum Vibrations in Molecules: A New Frontier in Computational Chemistry”

K. R. Glaesemann

26 January 2004

Final report summary of LDRD 02-LW-022 "Quantum Vibrations in Molecules: A New Frontier in Computational Chemistry"

Kurt R. Glaesemann
Lawrence Livermore National Laboratory

Purpose

With the trend towards needing information about chemistry at conditions significantly different from 298K and 1 atm., methods need to be developed to generate and interpret this data. This demand for information about chemistry at extreme conditions comes from many fields. The study of atmospheric chemistry requires knowledge of unusual species that are formed when molecules are exposed to ultraviolet radiation. Studying of energetic materials requires knowledge of the thermochemical and structural properties of a myriad of chemical species under a wide range of temperatures. Basic scientific understanding of the very nature of a chemical bond requires detailed information.

Studying these problems computationally requires multiple capabilities. The methodology used must provide both high accuracy and computational efficiency. Studying extreme chemistry also suffers from all the challenges of studying chemistry under non-extreme conditions. Therefore, either a new method must be developed or an old method must be applied in an innovative way.

The approach

The method we have chosen to use is path integral Monte Carlo (PIMC) for the nuclear degrees of freedom and ab initio electronic structure methods for the electronic degrees of freedom. PIMC and ab initio electronic structure are methods of treating the quantum nature of particles. These methods have been chosen, because an accurate treatment requires treating both the electrons and the nuclei as quantum particles. We developed new "projected" methods that reduce the computational demands. These methods along with PIMC in general are described in two Journal of Chemical Physics articles (UCRL-JC-144960 and UCRL-JC-147423). This methodology was implemented into a PIMC code developed as part of this LDRD. The code was parallelized in order to utilize the computational resources of LLNL.

Technical accomplishments

By coupling quantum treatment of the electrons via ab initio method to the quantum motion of the nuclei with PIMC, a method that is able to produce accurate results is obtained. This level of accuracy is necessary under extreme conditions, because traditional "empirical" corrections are not applicable under such conditions. Because the electronic structure is tightly coupled to the motion of the nuclei, ab initio methods must be used to treat the electrons. These methods have explicit molecular orbital dependence are not parameterized to simply reproduce an equilibrium geometry. This method can calculate structural information, energetics, and heat capacities. The thermochemical results are described in detail in a Journal of Chemical Physics article (UCRL-JC-149046).

Conclusion

A theoretical method must provide the level of accuracy needed to answer the question of interest; otherwise, the results could be potentially misleading. This methodology used in this LDRD provided both structural and energetic information. The method used provides a fully quantum approach to calculation properties of molecules under extreme conditions. The software to perform these calculations is written and is integrated with a variety of electronic structure codes (GAMESS and Fireball). The code incorporates new computer time saving methodologies. This method calculates the properties needed, such as energy and heat capacity. The code continues to be used after the completion of the LDRD.

Biography

K.R. Glaesemann and L.E. Fried, "An improved thermodynamic energy estimator for path integral simulations", J. Chem. Phys., 116, 5951-5955 (2002). UCRL-JC-144960.
K.R. Glaesemann and L.E. Fried, "Improved heat capacity estimator for path integral simulations", J. Chem. Phys., 117, 3020-3026 (2002). UCRL-JC-147423.
K.R. Glaesemann and L.E. Fried, "A path integral approach to molecular thermochemistry", J. Chem. Phys., 118, 1596-1603 (2003). UCRL-JC-149046.

About this document

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.